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Blending of styrene-*block*-butadiene-*block*-styrene copolymer with sulfonated vinyl aromatic polymers

Francesco Picchioni,[1] Ivan Giorgi,[2] Elisa Passaglia,[2] Giacomo Ruggeri[2]* and Mauro Aglietto[2]

[1]Polymer Technology Department of Chemical Engineering, SKT, Eindhoven University of Technology, Eindhoven, The Netherlands
[2]Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy

Abstract: Different polymers containing sulfonic groups attached to the phenyl rings were prepared by sulfonation of polystyrene (PS) and styrene-*block*-(ethylene-*co*-1-butene)-*block*-styrene (SEBS). The sulfonation degree (SD) was varied between 1 and 20 mol% of the styrene units.

Polyphase materials containing sulfonated units were prepared by blending styrene-*block*-butadiene-*block*-styrene (SBS), with both sulfonated PS and sulfonated SEBS in a Brabender mixer. Such a procedure was performed as an alternative route to direct sulfonation of SBS which is actually not selective towards benzene rings because of the great reactivity of the double bonds in polybutadiene (PB) blocks to sulfonation agents. Thermal and dynamic-mechanic analysis, together with morphology characterization of the blends, is consistent with obtaining partially compatible blends characterized by higher T_g of the polystyrene domains and improved thermal stability.

Keywords: sulfonation; SBS; SEBS; melt blending; thermal and dynamic behaviour

INTRODUCTION

Sulfonation has been widely used to graft polar groups onto macromolecular chains which are then able to self-interact by hydrogen bonding, and can also be neutralized, leading to the formation of sulfonate ionic groups. Ionic groups incorporated into a polymer have a decisive effect on its physical properties by giving rise to ionomeric domains.[1–4]

In particular, sulfonation has strong effects on thermal behaviour. In the case of sulfonated polysulfone[1,2] the presence of sodium sulfonate groups has a strong influence on T_g, which increases by as much as 130 °C. This demonstrates the importance of ionic intermolecular interactions in increasing T_g via an *ionomer effect*. Moreover, the thermomechanical behaviour can also be strongly influenced by the type of counterion of the sulfonate group: the rubber modulus (ie the modulus above the T_g of the polysulfone) increases on passing from mono- to divalent counterions, the degree of sulfonation (SD) remaining fixed.

Several scientific publications have been dedicated to polymers prepared by sulfonation of polystyrene (PS).[5–10] The morphology and microstructure of ionomers obtained by neutralizing the sulfonate groups, have been extensively studied to understand the influence of ionic aggregates on the thermomechanical behaviour. It has been found that the nature of the counterion does not influence the formation of ionic aggregates which can be arranged into multiplets when the SD is lower than 3 mol%, and into clusters for SD above 3 mol%. The microstructure of ionic aggregates depends on several factors, including the thermal history of the sample[11–13] and the presence of plasticizers.[14,15]

Furthermore, above the T_g of PS a plateau of E' is observed both for PS-SO_3H and PS-SO_3M samples, suggesting the presence of a network due to intermolecular hydrogen bonding and of ionic aggregates, respectively. The sulfonation reaction of styrene-*block*-(ethylene-*co*-1-butene)-*block*-styrene (SEBS) copolymer can be carried out by the same procedure as for PS.[16,17] Sulfonated and neutralized SEBS (SEBS-SO_3M) displays two glass transition temperatures for the 'hard' PS phase, while PS shows only a single T_g. Such behaviour has been explained by assuming the formation, in SEBS-SO_3M, of an ion-rich microphase that exists as a dispersed phase within PS domains.

The main objective of this paper is to induce an increase in the T_g and thermal stability (thermogravimetric analysis; TGA) of the hard phase of SBS by

* Correspondence to: Giacomo Ruggeri, Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy
E-mail: grugge@dcci.unipi.it
Contract/grant sponsor: Softer SpA, Forlì, Italy
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blending with sulfonated styrene polymers. Indeed PS-SO_3X (X=H, M) has a higher T_g and greater thermal stability (TGA) than PS. Clearly the effectiveness of this approach depends on the miscibility of PS-SO_3H with the PS domain and the presence of an ionomeric network.

Complete or partial miscibility can be hypothesized with different consequent properties (T_g). Complete miscibility would probably be less effective in reducing ionomeric interactions, particularly at low SD. On the contrary, more significant effects could be expected from partial compatibility of PS-SO_3X in the PS domains, which then show two phases strongly interfaced due to the presence in the PS-SO_3X ionic domains of relatively long PS blocks (Fig 1). In this case, we can expect that the T_g of the polybutadiene phase will not change significantly, while the hard phase will have two T_g values and exhibit increased thermal stability.

To test this hypothesis, the influence of polar aggregates on thermal properties and the component compatibility of SBS/PS-SO_3X and SBS/SEBS-SO_3X blends has been investigated by means of differential scanning calorimetry (DSC), thermomechanical analysis (TMA), dynamic mechanical thermal analysis (DMTA) and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

SEBS triblock copolymer (Kraton G-1650) containing 19 mol% of styrene, with $\overline{M}_n = 8.0 \times 10^4$ g mol^{-1} and $\overline{M}_w/\overline{M}_n = 1.2$–1.5, atactic PS (Repsol) with $\overline{M}_n = 5.2 \times 10^3$ g mol^{-1} and $\overline{M}_w/\overline{M}_n = 2.5$, and SBS triblock copolymer (Calprene 501) were used without further purification. SBS has a butadiene/styrene ratio of 69/31 (w/w) with block average molecular weight 9300–41 400–9300 g mol^{-1}, $\overline{M}_w/\overline{M}_n = 1.5$ and a 10 wt% content of vinyl units in the butadiene block. From the average molecular weight and the weight percentage of styrene in the SEBS copolymer, the lengths of styrene and ethylene/1-butene blocks can be calculated as 7500 and 65 000 g mol^{-1}, respectively.

Sulfuric acid 96% (Ashland), *para*-toluene sulfonic acid 98% (Aldrich), acetic anhydride (Carlo Erba), 1,2-dichloroethane (Carlo Erba), toluene (Carlo Erba), isopropanol (Carlo Erba), Al(O^iPr)$_3$ (Sigma), LiOH (Carlo Erba), NaOH (Carlo Erba), KOH (Carlo Erba) and $Zn(OAc)_2 \cdot 2H_2O$ (Rudipont) were used without further purification.

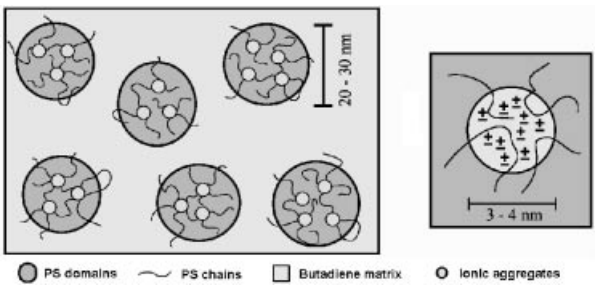


Figure 1. Schematic representation of ionic aggregates in SBS–PS-SO_3X blends.

Sulfonation of PS and SEBS

The sulfonation method is analogous to that described by Weiss *et al*[12,13] and a standard procedure is as follows: fixed amounts of 1,2-dichloroethane (1,2-DCE) and acetic anhydride were introduced into a 25 ml Schlenck flask under dry nitrogen atmosphere, and after cooling at 0 °C a concentrated solution of sulfuric acid was added. The solution was stirred until it became homogeneous and then heated slowly to room temperature. Acetyl sulfate was freshly prepared for each run, even if only a calculated fraction of the total amount was used.

Calculated amounts of solvent (1,2-DCE) and polymer (PS or SEBS) were introduced into a two-necked flask equipped with a magnetic stirrer and a reflux condenser, heated at 60 °C and the mixture degassed by purging with dry nitrogen for 15 min. A calculated amount of acetyl sulfate was then added and the reaction mixture left for 2 h at 60 °C under stirring. The reaction was interrupted by adding an excess of 2-propanol in 30 min and then cooled to room temperature.

The reaction mixture was purified by precipitation in a 20-fold excess of water directly in a necked flask equipped with a reflux condenser. The obtained white colloidal suspension was left for 2 h at 100 °C under stirring. The mixture was then slowly cooled to room temperature and the polymer was recovered by filtration, suspended in a small amount of ethanol and dried under reduced pressure (about 1 mmHg) at 50 °C for 5 days.

Sulfonation degree (SD) determination

The SD of all samples was determined by titration with methanolic NaOH. A 0.006 M NaOH solution was prepared and standardized by weighed amounts of *p*-toluene sulfonic acid in methanol solution using phenolphthalein as indicator. All titrations were performed by dissolving the polymer (200 mg) in a toluene–methanol mixture; the volume ratio was fitted in order to achieve complete solubility of the sulfonated samples.

Neutralization of sulfonated polymers

All sulfonated polymers were neutralized by means of several inorganic bases following the same procedure. The sample was dissolved in a toluene–methanol mixture (9/1 v/v) and then a molar excess of the inorganic base (1.2/1.0 by mol with respect to sulfonic acid groups) was added. The composition of the solvent mixture was adjusted to avoid precipitation of the polymer. The homogeneous solution was left under stirring for 2 h after which the solvents were evaporated under reduced pressure. The residual solid was then suspended in water at 60 °C and left for 2 h under stirring. The polymer was filtered and dried

under reduced pressure (about 1 mmHg) at 50 °C for 7 days, giving samples of PS-SO_3M and SEBS-SO_3M.

Preparation of SBS/sulfonated polymer blends

All blends (see Tables 2 and 4 for detailed lists) were prepared under nitrogen atmosphere by introducing the desired amounts of the components into a Plastograph Brabender mixer at 180 °C, rotor speed 50 rev min^{-1}. After the desired time of residence (10 min), the mixing was stopped and the materials recovered from the mixer.

Characterization of polymer blends

FT IR analysis

Infrared spectra were recorded with a Fourier transform spectrometer (Perkin Elmer FTIR 1750) on films cast from solvent solution on KBr windows, or by deposition of a drop of liquid between two KBr windows.

Differential scanning calorimetry

DSC analyses were performed by a Perkin Elmer DSC7 calorimeter equipped with a CCA7 cooling device. The calibration was carried out by using mercury (mp −38.4 °C) and indium (mp 156.2 °C) standards for low-temperature scans and indium and zinc (mp 419.5 °C) for high-temperature scans. To remove any low-molecular weight impurity that could still have been present in the samples after drying, DSC runs were performed using DSC pans with a small hole on the top. Heating and cooling thermograms were recorded at a standard rate of 20 °C min^{-1} up to a maximum temperature of 250 °C. T_g values were measured from the second heating run.

Thermogravimetric analysis

All TGA thermograms were recorded by a Mettler TC11 instrument equipped with a Mettler M3 balance with an accuracy of 10^{-3} mg. Heating was performed at a standard rate of 10 °C min^{-1} under dry nitrogen.

Scanning electron microscopy

All scanning electron micrographs were recorded on cryogenic fracture surfaces by a Jeol JSM model T-300 instrument at the Chemical Engineering Department of Pisa University.

Dynamic mechanical thermal analysis

Thermograms were recorded using a Perkin Elmer DMA7e instrument (three-point bending geometry). Thermograms were recorded at a standard heating rate of 1 °C min^{-1}.

Thermomechanical analysis

All TMA thermograms were recorded with a Perkin Elmer TMA7 instrument.

RESULTS AND DISCUSSION

Sulfonation of PS and SEBS

Sulfonated polystyrene (PS-SO_3H) and SEBS (SEBS-SO_3H) were prepared with various contents of sulfonic acid groups. The SD (ratio between sulfonated styrene repeating units and total styrene units) was evaluated by titration of toluene–methanol 9:1 v/v mixtures with a 0.006 M solution of sodium hydroxide in methanol using phenolphthalein as indicator. The reaction is quantitative with respect to acetyl sulfate for low SD values (up to 3 mol%) but the yield decreases (Fig 2) for higher values. This behaviour was explained by taking into account the electron withdrawing effect of the sulfonic acid group grafted onto the phenyl ring of the styrene units. 1,2-DCE is a good solvent for SEBS, at least from a macroscopic point of view, giving an apparently homogeneous solution. However, SEBS seems to be less reactive than PS as depicted in Fig 2.

All sulfonated samples (PS-SO_3H and SEBS-SO_3H) display a single glass transition temperature (Table 1), thus suggesting that polar sulfonic acid groups are not segregated but dispersed within the PS domains. The T_g increases with increasing SD: the effect is more evident for PS than for SEBS (but it must be taken into account that SD for SEBS is only related to the PS phase which corresponds to 30 wt% of the entire copolymer). Moreover, the T_g of the copoly(ethylene/1-butene) phase (for sulfonated SEBS) does not change upon sulfonation: this behaviour can be related to the high selectivity of acetyl sulfonate towards the benzene ring.[16,17] Both PS-SO_3M and SEBS-SO_3M salts display higher T_g values. Actually, the latter displays two glass transitions (T_g^2 and T_g^3 in Table 1) which can be related to the coexistence of a PS phase with low ion content, and of a second PS phase with higher ion content, respectively.[17] It is not possible to completely exclude that the salts of sulfonated PS may also display two T_g transitions with only one detectable by DSC analysis. Furthermore, both T_g^2 of PS-SO_3M and T_g^3 of SEBS-SO_3M increase with the Lewis-acid strength of the cation and with the first-shell coordination number, thus suggesting that the more sulphonate groups

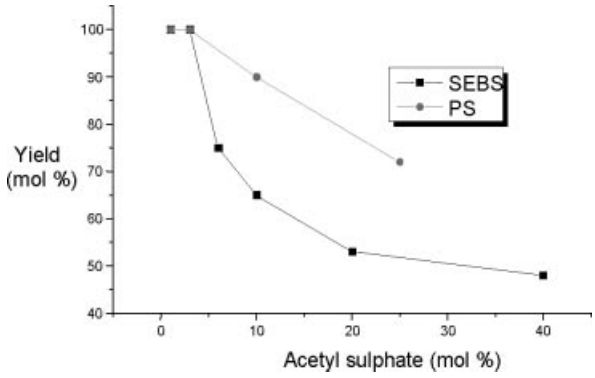


Figure 2. Yield of sulfonation for polystyrene (PS) and styrene-*block*-(ethylene-*co*-1-butadiene)-*block*-styrene (SEBS).

Table 1. Thermal behaviour of sulphonated polystyrene (PS) and styrene-*block*-(ethylene-*co*-1-butadiene)-*block*-styrene (SEBS)

Run	SD (mol%)[a]	T_d (°C)[b]	T_g^1 (°C)[c]	T_g^2 (°C)[c]	T_g^3 (°C)[c]
PS	0.0	383.7	–	87.5	–
PS-SO_3H	1.0	404.8	–	89.8	–
PS-SO_3H	3.0	402.5	–	90.1	–
PS-SO_3H	9.0	397.5	–	107.7	–
PS-SO_3H	18.0	383.0	–	101.8	–
PS-SO_3Li	3.0	397.7	–	99.5	–
PS-SO_3Na	3.0	395.3	–	99.4	–
PS-SO_3K	3.0	395.3	–	92.4	–
PS-SO_3Zn	3.0	–	–	103.5	–
PS-SO_3K	1.0	390.7	–	89.3	–
PS-SO_3K	9.0	344.0	–	121.2	–
PS-SO_3K	18.0	388.3	–	233.9	–
SEBS	0.0	421.0	–52.4	81.4	–
SEBS-SO_3H	1.0	432.5	–51.8	89.7	–
SEBS-SO_3H	3.0	435.7	–52.7	90.3	–
SEBS-SO_3H	6.5	440.3	–51.6	90.0	–
SEBS-SO_3H	10.0	438.0	–50.9	91.4	–
SEBS-SO_3H	19.0	450.0	–54.4	96.0	–
SEBS-SO_3Li	6.5	420.7	–54.4	90.0	149.9
SEBS-SO_3Na	6.5	421.0	–52.7	90.7	nd[d]
SEBS-SO_3K	6.5	423.3	–53.5	91.5	nd[d]
SEBS-SO_3Zn	6.5	420.7	–54.0	92.4	154.8
SEBS-SO_3Al	6.5	420.7	–53.3	92.7	158.1

[a] Determined by titration.
[b] Evaluated as upturn point of 1st derivative TGA curve.
[c] Evaluated from 2nd heat DSC curve.
[d] Not determined.

linked to the cation, the higher the hindrance to chain mobility.

The presence of polar groups greatly improves the thermal stability of the sulfonated samples, as can be seen from TGA data. The degradation temperature

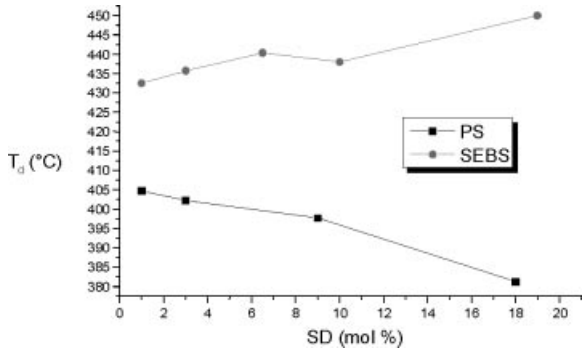


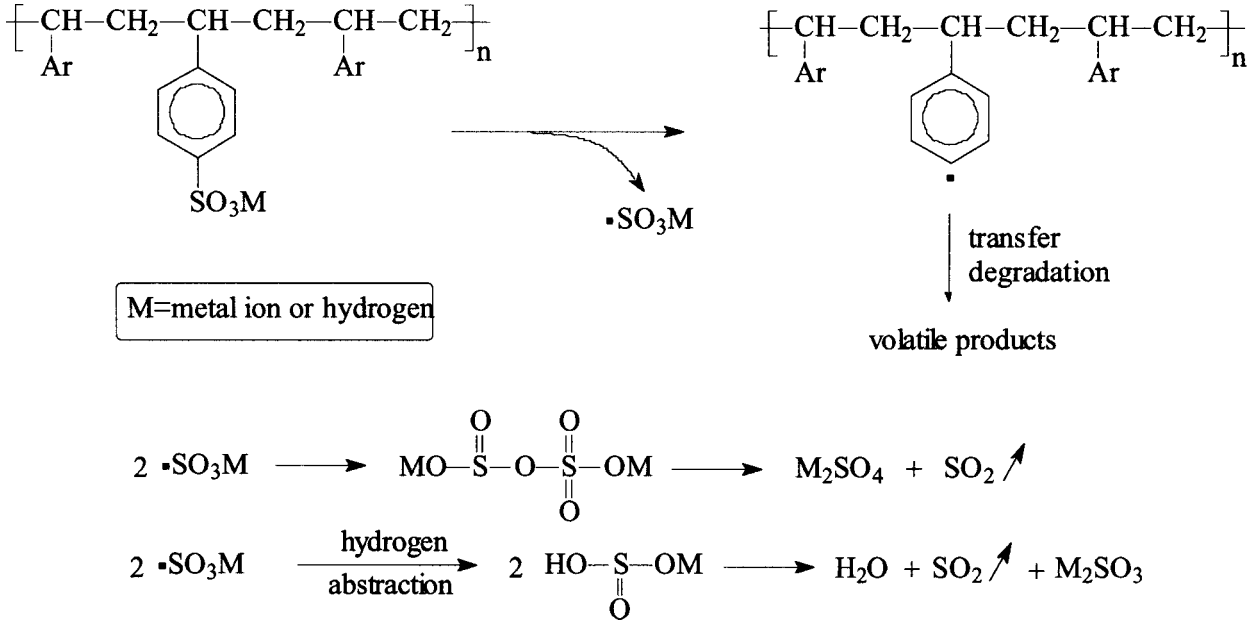
Figure 3. Degradation temperatures of PS-SO_3H and SEBS-SO_3H samples.

(T_d), evaluated as the upturn point of the derivative curve, depends on SD in a different way for the homopolymer and the copolymer (Fig 3). Such behaviour can be explained by assuming that, depending on the local concentration of sulfonate groups and on the morphology of the sample, alternative degradation pathways are operative,[18] which do not occur in simple PS. Such a mechanism involves loss of SO_2, and its occurrence is strictly dependent on the local concentration of $\cdot SO_3M$ radicals (Scheme 1).

Blends of sulfonated PS with SBS

Styrene–butadiene–styrene (SBS) triblock copolymers cannot be sulfonated selectively at the styrene repeating units as described above for PS and SEBS because of the presence of double bonds in the PB phase which are strongly reactive towards sulfonating agents such as acetyl sulfate. The mixing of SBS with sulfonated PS or SEBS represents an alternative pathway which allows polar groups to be introduced into the material.

Thus, blends of SBS were prepared with 5, 10 and 15 wt% of PS, PS-SO_3H (SD = 3 mol%) and PS-SO_3K



Scheme 1. Proposed pathway of degradation for strongly sulfonated samples.

Table 2. DSC analysis of styrene-*block*-butadiene-*block*-styrene (SBS) (sulfonated) polystyrene (PS) blends

Run[a]	T_g^1 (°C)[b]	T_g^2 (°C)[b]	T_g^3 (°C)[b]
SBS	−84.5	80.8	–
PS	–	87.5	–
PS-SO_3H[c]	–	87.4	–
PS-SO_3K[c]	–	92.4	–
SBS/PS 95/5	−86.4	91.5	–
SBS/PS 90/10	−87.5	95.3	–
SBS/PS 85/15	−88.1	99.6	–
SBS/PS-SO_3H 95/5	−86.3	89.8	–
SBS/PS-SO_3H 90/10	−87.7	88.1	–
SBS/PS-SO_3H 85/15	−86.4	90.8	–
SBS/PS-SO_3K 95/5	−87.1	96.0	112.0
SBS/PS-SO_3K 90/10	−87.3	96.0	112.0
SBS/PS-SO_3K 85/15	−87.2	96.0	112.0

[a] Blend composition is expressed in weight ratios.
[b] Evaluated from 2nd heat DSC thermograms.
[c] SD = 3 mol%.

(SD = 3 mol%), respectively. All blends display (Table 2) glass transition temperatures for the polybutadiene phase which are very similar to those of SBS, thus suggesting that only small amounts of PS, PS-SO_3H and PS-SO_3K are located in this phase. The T_g values of PS domains are higher than those of the corresponding pure components, thus confirming the presence of a synergistic effect, as reported for solution-cast blends of PS and SBS.[19,20] Blends of SBS with PS or PS-SO_3H display a single glass transition temperature for the PS phase, indicating good compatibility between the components. Moreover, PS seems more effective than PS-SO_3H, because the T_g values for SBS–PS blends are higher than those of SBS/PS-SO_3H blends over the entire composition range.

SBS/PS-SO_3K blends display two glass transition temperatures for the 'hard phase', 16 °C and 32 °C higher, respectively, than the same phase of SBS. According to T_g indications, scanning electron micrographs (Fig 4) of SBS/PS blends show a homogeneous morphology (SBS/PS 95/5) with moderate phase separation (white spots) with increasing PS content (SBS/PS 85/15). In the case of SBS/PS-SO_3H blends, this last effect is more evident than in the previous case.

Evident phase segregation occurs for SBS blends with PS-SO_3K, where white domains are spread in the dark matrix and located in cavities without apparent adherence to the matrix. These domains correspond to a PS phase with high concentration of K-neutralized sulfonate groups. Scanning electron microanalysis clearly shows a maximum of potassium concentration inside the white domains. All samples display improved thermal stability as a function of blend composition (Fig 5): this result is quite surprising considering that all PS components have a lower thermal stability than SBS (Table 1). TGA data indicate that the net change in thermal stability can then be evaluated as an improvement of about 10–15 °C for all blends.

The thermo-mechanical behaviour of SBS triblock copolymer is also significantly modified upon melt mixing with PS and sulfonated PS (Table 3) in agreement with DSC data. For SBS/PS blends, the softening temperature T_s increases monotonously with PS content up to 117 °C for the 85/15 blend. The same trend holds for blends with sulfonated PS, even if the variations are smaller; for the SBS/PS-SO_3K blends the maximum (T_s = 121 °C) is reached for a composition of 90/10 by weight.

The observed results can be rationalized by considering the mutual solubility of the added component into the PS domains of SBS, as already proposed for SBS–PS blends.[19–21]

In our case, because the molar mass of polystyrene blocks in the terpolymer and that of the PS homopolymer are close to each other, the key parameter determining the solubility could be also the difference in polarity between the PS chains of SBS and modified PS chains of the sulfonated polymer. This hypothesis is confirmed by DSC and SEM data, which clearly show the stiffening of the PS phase (T_g increment) and the formation of a new phase (macrophase separation) with increasing PS contents in the PS domains of SBS, and also the polarity of the PS component. In fact, SBS/PS-SO_3K blends (the neutralized component is the most polar among those mixed with SBS) display very low solubility of sulfonated component in SBS: in this case the formation of two different PS phases with two glass transition temperatures is observed. Moreover, the two corresponding T_g values are still above those of the PS domains in SBS because of the high rigidity of the ionomer phase and of the low, but still appreciable, number of entanglements formed during melting.

The same observations have been made for SBS/PS-SO_3H blends: the low level of sulfonation allows one single hard phase to be obtained which shows improved thermal behaviour over neat SBS. The effect is less marked, probably because of either lower solubility of the sulfonated PS component in the PS domains or a lower number of polar groups grafted on the sulfonated component.

Blends of SBS with sulfonated SEBS

Like sulfonated PS, sulfonated SEBS has never previously been employed in melt mixing with SBS. Therefore the blends SBS/SEBS, SBS/SEBS-SO_3Zn and SBS/SEBS-SO_3Al were prepared with variable SEBS contents of 5, 10 and 15 wt%, respectively. All sulfonated materials are characterized by an SD value of 6.5 mol% (with respect to the PS block). DSC analysis shows (Table 4) in all cases the presence of a single transition (for the hard phase), thus suggesting good compatibility between the hard phase of SBS and SEBS sulfonated samples, as is also confirmed by scanning electron micrographs (Fig 6). For all blends, the T_g does not seem to depend on the content of

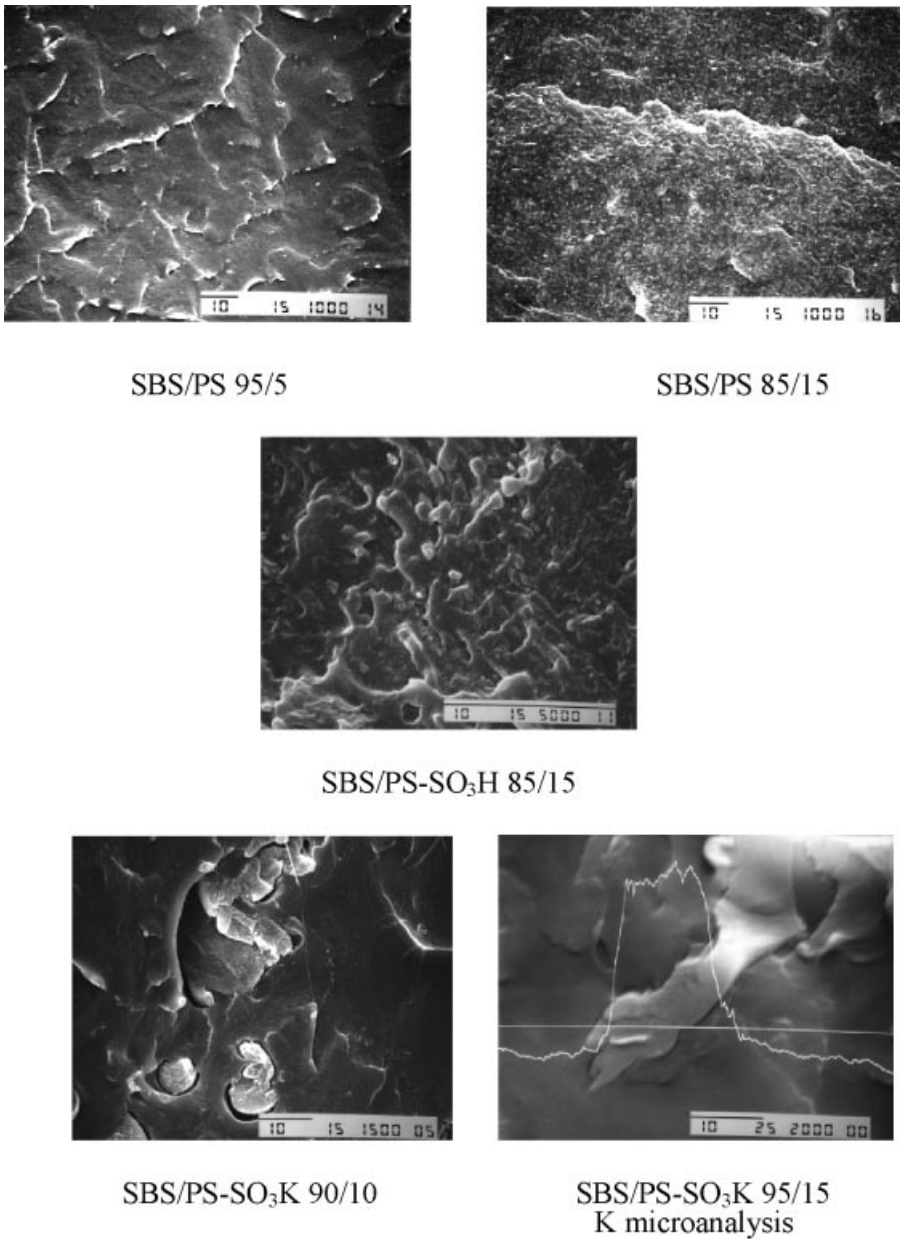


Figure 4. SEM analysis of SBS/PS, SBS/PS-SO_3H and SBS/PS-SO_3K blends.

sulfonated component and is very close to those of the pure copolymers, which are characterized by very similar thermal behaviour. This effect could be due to

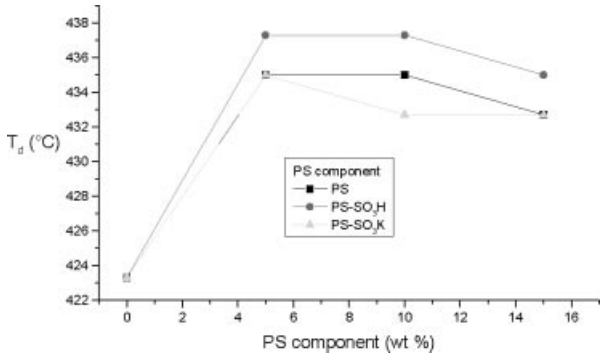


Figure 5. T_d as a function of blend composition.

Table 3. TMA of styrene-*block*-butadiene-*block*-styrene (SBS)/(sulfonated) polystyrene (PS) blends

Run[a]	T_g (°C)[b]
SBS	104
SBS/PS 95/5	113
SBS/PS 90/10	113
SBS/PS 85/15	117
SBS/PS-SO_3H 95/5	107
SBS/PS-SO_3H 90/10	112
SBS/PS-SO_3H 85/15	114
SBS/PS-SO_3K 95/5	107
SBS/PS-SO_3K 90/10	121
SBS/PS-SO_3K 85/15	113

[a] Blend composition is expressed in weight ratios.
[b] Evaluated as inflection point of TMA thermograms.

Table 4. DSC analysis of styrene-*block*-butadiene-*block*-styrene (SBS)/(sulphonated) styrene-*block*-(ethylene-*co*-1-butadiene)-*block*-styrene (SEBS) blends

Run[a]	T_g (°C)[b]
SBS	80.8
SEBS	81.8
SEBS-SO_3Zn	92.4
SEBS-SO_3Al	92.7
SBS/SEBS 95/5	79.7
SBS/SEBS 90/10	86.4
SBS/SEBS 85/15	81.6
SBS/SEBS-SO_3Zn 95/5	78.9
SBS/SEBS-SO_3Zn 90/10	79.8
SBS/SEBS-SO_3Zn 85/15	82.1
SBS/SEBS-SO_3Al 95/5	82.1
SBS/SEBS-SO_3Al 90/10	82.5
SBS/SEBS-SO_3Al 85/15	83.1

[a] Blend composition is expressed in weight ratios.
[b] Evaluated from 2nd heat DSC thermograms.

the very low content of sulfonated groups (0.9 mol%) in SEBS-SO_3M.

In any case, the dynamic behaviour of SBS triblock copolymer is only slightly modified by melt blending with sulphonated SEBS (Table 5). Both tanδ and T_g values for all blends show very similar trends to those outlined in the discussion of DSC data. However, all blends display only one single transition for the hard phase, thus confirming that good compatibility has been achieved.

Table 5. DMTA of styrene-*block*-butadiene-*block*-styrene/styrene-*block*-(ethylene-*co*-1-butadiene)-*block*-styrene (SBS/SEBS) blends

Run[a]	T_g (°C)[b]	tanδ (°C)
SBS	64.6	78.2
SEBS	83.2	93.3
SBS/SEBS 95/5	67.9	80.0
SBS/SEBS 90/10	67.6	83.8
SBS/SEBS 85/15	68.7	83.7
SBS/SEBS-SO_3-Al 95/5	68.0	83.9
SBS/SEBS-SO_3-Al 90/10	74.5	85.4
SBS/SEBS-SO_3-Al 85/15	73.6	88.6
SBS/SEBS-SO_3-Zn 95/5	71.8	84.5
SBS/SEBS-SO_3-Zn 90/10	72.8	87.3
SBS/SEBS-SO_3-Zn 85/15	77.3	91.0

[a] Blend composition is expressed in weight ratios.
[b] Evaluated as onset of DMTA curve.

CONCLUSIONS

The formation of macromolecular ionic complexes by neutralization of phenyl sulfonic groups allows the thermal behaviour of both PS and SEBS to be modified, thus increasing the glass transition temperature. Moreover, T_g is strongly dependent on the SD value and on the chemical nature of the cation. Indeed, cations such as Al^{3+} and Zn^{2+}, which allow an increase of the coordination number in the first shell up to three, give higher T_g values because of their high Lewis-acid strength and multiple crosslinking.

Like PS, sulfonated PS and SEBS can also be blended with the SBS triblock copolymer, with permanence of a hard phase having T_g value(s) higher

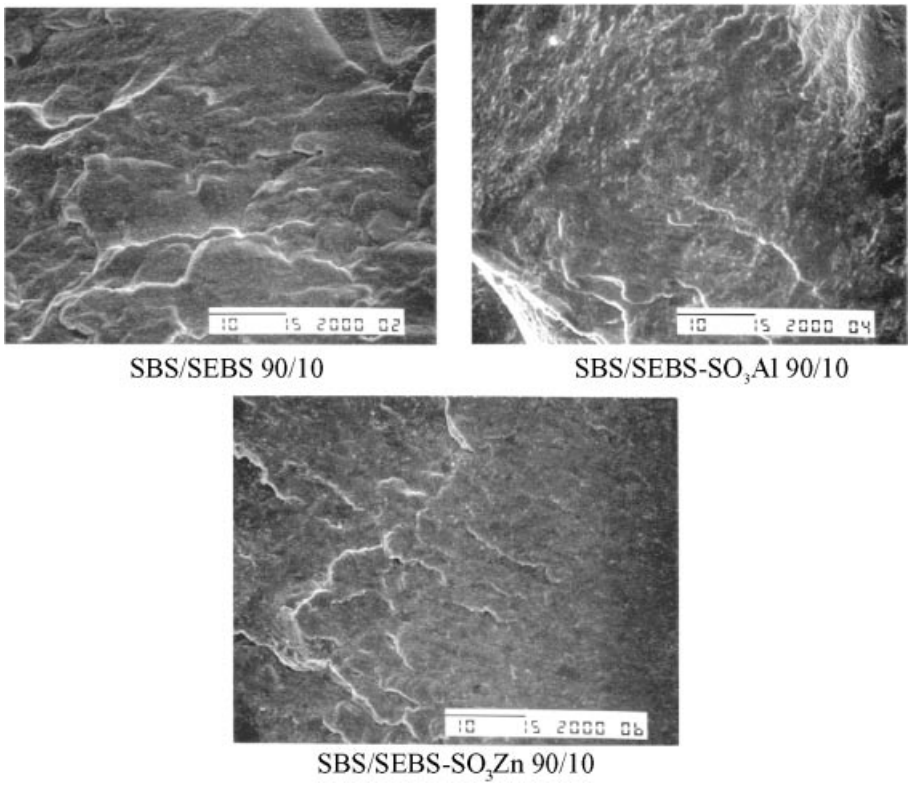


Figure 6. SEM analysis of SBS/(sulphonated) SEBS blends.

than the broad T_g of SBS. The control of SD allows compatibility of the sulfonated component with the styrene blocks of the SBS macromolecules, and this also depends, on the chemical nature of the cation. In any case, hard monophase or biphase domains are formed which are characterized by one or two T_g values, both higher than the T_g of pristine SBS. DSC and DMTA demonstrate that a synergic effect occurs in SBS–PS blends and also in those with sulphonated PS. This behaviour can be explained on the basis of significant compatibility of the added component into SBS, and of the morphological structure that can be formed upon melt mixing.

Only partial compatibility can be obtained when the sulfonic groups are neutralized with strong cations (K^+). Indeed, with increasing polarity and/or weight content of the PS component, it is possible to observe phase segregation that is 'micro dispersed' for blends of SBS with pure PS or PS-SO_3H, but is more evident for SBS/PS-SO_3K blends.

A low SD value (3 mol% of sulfonic units) and a strong counterion (K^+) were selected to optimize the thermal behaviour improvement of the blend and compatibility between the components.

In the case of sulfonated SEBS, the aluminium salt also displays a significant thermal improvement, but is characterized by a more pronounced microphase separation. The zinc salt shows a similar thermal effect with nearly complete solubility of the sulfonated component in PS domains of SBS.

With reference to the models proposed in the Introduction concerning the possible organization of sulfonated styrene polymers in the hard aromatic domains of SBS, the reported data confirm that a more substantial increase of the thermal properties is reached when incomplete dispersion of the sulfonated phenyl units allows the formation of ionomeric interactions in the hard phase of the blended SBS. More work will be necessary to better rationalize these results and detect the best values which can be reached by proper selection of the ionomeric polymers blended with SBS.

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